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EQUILIBRIUM DISTRIBUTION COEFFICIENTS FOR EXTRACTION OF ORGANIC PRIORITY POLLUTANTS FROM WATER - I

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16. ABSTRACT

Equilibrium distribution coefficients have been determined for extraction of acrolein, acrylonitrile, N-nitrosodimethylamine, isophorone, 2-chlorophenol, bis(2-chloroethyl) ether, bis(2-chloroethoxy) methane, phenol, resorcinol, pyrogallol, and nitrobenzene from water into a variety of solvents including paraffins, aromatics, ketones, esters, ethers, phosphates, chlorinated hydrocarbons, alcohols, carboxylic acids, and amines. These results are interpreted in terms of Lewis-acid, Lewis-base concepts.

Equilibrium distribution coefficients are also measured for extraction of benzene, toluene, ethylbenzene, chlorobenzene, 1-2 dichloroethane, 1-1-1 trichloroethane, 1-1-2-2 tetrachloroethane, 1-2 dichloropropane, 1-2 transdichloroethylene, trichloro-ehtylene, tetrachloroethylene, and bromoform from water into undecane, modeling kerosene as a solvent. In all cases, values of distribution coefficient are high enough to make extraction into kerosene an attractive removal process.

Vapor-liquid equilibrium data and results of 72-hour stability tests are reported for mixtures of acrolein or acrylonitrile with several candidate solvents. On the basis of the experimental results likely attractive solvents are identified.

Conceptual process designs and economic analyses are carried out for a number of solvent/solute systems, and result in projected costs (1982 dollars) of $1.10 to $3.20 per m^3 of water for removal of solutes present at 200 to 1000ppm levels in water.

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FOREWORD

The Environmental Protection Agency is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise, and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life. In partial response to these mandates, the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, is charged with the mission to manage research programs to investigate the nature, transport, fate, and management of pollutants in ground water and to develop and demonstrate technologies for treating wastewaters with soils and other natural systems for controlling pollution from irrigated crop and animal production agricultural activities; for developing and demonstrating cost-effective land treatment systems for the environmentally safe disposal of soild and hazardous wastes.

This report presents the basic information and procedures for development of solvent extraction techniques to remove a number of the priority pollutants from wastewaters at their source, thereby preventing entry into the environment at diluted levels. Early removal from lower wastewater volumes prevents the risks of broadening the exposure to the pollutants and ameliorates the technical and economic problems associated with cost-effective removal or treatment of low concentrations in large volumes of wastewater.

Volume I presents the data for halogenated hydrocarbons and aromatics, phenols, acrolein, acrylonitrile, and nitrobenzene. Volume II includes additional distribution coefficient data plus conceptual designs and process economics projections.

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ABSTRACT

Equilibrium distribution coefficients (K_D) were measured for extraction of a number of organic EPA Priority Pollutants from water into various solvents. Data are presented for extraction of benzene; toluene; ethylbenzene; chlorobenzene; 1,2-dichloroethane; chloroform; carbon tetrachloride; 1,1-dichloroethane; 1,2-dichloroethane; 1,1,1-trichloroethane; 1,1,2,2-tetrachloroethane; 1,2-dichloropropane; 1,2-*trans*-dichloroethylene; trichloroethylene; tetrachloroethylene; and bromoform into undecane, modeling kerosene as a solvent. In all cases values of K_D are high enough to make extraction into kerosene an attractive removal process.

Data are also presented for extraction of phenol, resorcinol, pyrogallol, 2-chlorophenol, 2-nitrophenol, acrolein, acrylonitrile, and nitrobenzene from water into a variety of solvents, including undecane, toluene, tributyl phosphate (TBP), methyl isobutyl ketone (MIBK), diisobutyl ketone (DIBK), trioctyl phosphine oxide (TOPO) and a number of other substances. Combinations of acidic solutes with basic solvents, and *vice versa*, give enhanced values of K_D, which it should be possible to exploit through lower solvent-to-water ratios in an operating process.

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SECTION 1

INTRODUCTION

The U. S. Environmental Protection Agency has established a list of 129 Priority Pollutants, upon which primary emphasis is being placed for development of reliable and precise analytical techniques and evaluation of appropriate control technology. This information serves as necessary background for the identification of the Best Available Control Technology Economically Achievable (BATEA). More information on the Priority Pollutants and this general effort is provided by Keith and Telliard (1979).

Although not yet one of the most common approaches used as control technology, solvent extraction holds good potential for removal of many of the organic Priority Pollutants from effluent water streams. Solvent extraction can be attractive in cases where the solutes in question are toxic or non-biodegradable, where the solutes are present at high enough concentrations to provide economic recovery value and/or when steam stripping would be complicated or precluded by low solute volatility and/or formation of azeotropes with water. Solvent extraction can also be a broad-brush removal process for dissolved organics in cases where an inexpensive solvent gives large equilibrium removals of the spectrum of solutes present. Solvent extraction has been used for many years for recovery of phenols from aqueous effluents from coke ovens in the iron-and-steel industry, and is a likely component of processing systems for condensate waters from coal gasification or liquefaction.

The purpose of this project is to establish phase-equilibrium data necessary for evaluation of solvent extraction as a treatment and/or recovery process for a large number of the organic Priority Pollutants in aqueous streams. The principal piece of information sought has been the equilibrium distribution coefficient, K_D, defined as the weight fraction of solute in the solvent phase divided by the weight fraction of solute in the aqueous phase, at equilibrium

and at high dilution. Higher values of K_D lead to less solvent flow being required in proportion to the water flow rate, and thereby usually lead to less expensive extraction processes, provided that solvent regeneration can be achieved economically.

The present report provides information on K_D for chlorinated hydrocarbons, aromatics, phenols, bromoform, 2-chlorophenol, acrolein, acrylonitrile and nitrobenzene, for extraction from water into kerosene and/or other solvents as appropriate. Volume II provides information on K_D for other solutes, as well as conceptual designs and cost estimates.

SECTION 2

CONCLUSIONS

Equilibrium distribution coefficients for extraction of the chlorinated hydrocarbons and aromatic hydrocarbons into undecane were all high enough to make kerosene an attractive solvent for removal of these compounds from water by solvent extraction.

For the more polar solutes investigated (phenol, resorcinol, pyrogallol, 2-chlorophenol, 2-nitrophenol, acrolein, acrylonitrile, and nitrobenzene), equilibrium distribution coefficients into hydrocarbon solvents are lower than those into weak or moderately strong complexing extractants, which can interact with the solute through Lewis acid-Lewis base mechanisms. For phenol and polyhydic and substituted phenols, methyl isobutyl ketone (MIBK) is an effective low-boiling solvent, while trioctyl phosphine oxide (TOPO) in diluents such as diisobutyl ketone (DIBK) is a strong high-boiling extractant. For nitrobenzene, DIBK is an effective low-boiling solvent, giving somewhat higher K_D than MIBK. Tributyl phosphate (TBP) is an effective high-boiling solvent for nitrobenzene, and probably also for phenols. In cases where the ketones are effective solvents, acetates are also effective, giving somewhat lower values of K_D than the ketones.

SECTION 3

RECOMMENDATIONS

The more promising solvents noted in the previous section are worthy of further investigation through conceptual designs of solvent extraction processes for removal of various pollutants and combinations of pollutants from water. These designs should include considerations of solvent regeneration, solvent stability, heat exchange, and net solvent consumption.

SECTION 4

SOLVENT SELECTION STRATEGY

Important factors influencing the selection of solvents are the size of the equilibrium distribution coefficient (K_D); the solubility of the solvent in water (and ease of recovering it if it is too soluble); ease and completeness of regeneration; stability over long periods of time in contact with the aqueous stream in question; toxicity; viscosity; difference in density from water; interfacial tension and lack of emulsion tendencies with water; and cost. For processing large volumes of water these considerations lead rather directly to the use of kerosene or another hydrocarbon solvent, provided it gives sufficiently high equilibrium distribution coefficients for the solute(s) of interest. Kerosene was therefore the principal solvent investigated for solutes, such as chlorinated hydrocarbons and aromatics, which would give high values of K_D for extraction into kerosene.

Regeneration of a solvent is frequently accomplished by distillation, especially if the solvent flow rate can be kept low enough to hold down the energy costs for distillation. In most cases kerosene would be sufficiently higher boiling than the solute(s) of interest so that distillation would be simple. In cases where the solute boiling point is close to that of kerosene, a hydrocarbon solvent of different molecular weight can be considered.

For more polar organics, kerosene usually does not give a high enough value of K_D to be attractive. In those cases other solvents were considered, chosen through the guidelines mentioned above.

Tricresyl phosphate (TCP) was considered as one alternative solvent in the early parts of this project, and it does provide high values of K_D in many cases. However, the triaryl phosphates were found to be subjects of concern with regard to neurotoxicological effects upon fish and other species. For that reason TCP is considered inadvisable as a solvent for water treatment and was therefore not considered further.

In some cases, high values of K_D can be achieved through the use of a chemical extractant, which forms a reversible intermolecular complex with the solute. Such extractants can be desirable from the standpoints of both capacity and selectivity for one solute over others. They are usually more costly than the more common solvents, but their better performance can offset the cost disadvantage.

With complexing extractants it is frequently desirable to blend the extractant with an organic diluent in a solvent mixture. There can be several reasons for doing this, including dissolution of the extractant if it is a solid, adjustment of the density difference between phases, reduction of solvent viscosity, and/or letting the diluent provide most of the solvent volatility in the reboiler of a distillation column used for regeneration of the solvent mixture. Another incentive for using a diluent in several cases is that higher values of K_D can be achieved with the mixed solvent than with either the extractant or the diluent alone. Wardell and King (1978) and Ricker and King (1979) give examples of such behavior for the extraction of acetic acid from water using tertiary amines and phosphine oxides as complexing extractants.

An important distinction should be made between low-boiling and high-boiling solvents. A high-boiling solvent is defined as one having a higher boiling point than the solute(s) being extracted. With such a solvent the extracted pollutants will go overhead in a distillation column used for solvent regeneration, whereas with a solvent having a lower boiling point than the solute(s) the solvent will go overhead. Since the solvent is usually by far the major constituent of the loaded solvent mixture, the use of a high-boiling solvent usually leads to less energy consumption, since less boil-up is required to generate the smaller distillate. However, use of a high-boiling solvent can lead to high reboiler temperatures in a distillation column used for regeneration, with resulting thermal degradation and/or significant sensible heat requirements. Furthermore, with a high-boiling solvent there can be a problem of build-up

of non-volatile contaminants in the recirculating solvent stream, making a purge necessary, with solvent loss and/or need for additional processing of the purge.

Since the factors favoring high-boiling and low-boiling solvents relative to one another are specific to the individual processing situation, it is desirable to identify attractive solvents within both classes.

SECTION 5

EXTRACTION OF HALOGENATED HYDROCARBONS AND AROMATICS INTO UNDECANE

The halogenated hydrocarbons and aromatic hydrocarbons on the EPA Priority Pollutant list give high equilibrium distribution coefficients into kerosene, and therefore kerosene is likely to be the most attractive broad-brush solvent for removal of these compounds. Since kerosene itself is a mixture of many components of different molecular weight, and since the proportions in that mixture can vary, the measurements of K_D for chlorinated hydrocarbons and aromatics were carried out using n-undecane as the solvent. n-Undecane has a boiling point midway in the kerosene range.

EXPERIMENTAL METHODS

For these solutes the high volatilities in aqueous solution provided special problems, and the experimental methods were designed to minimize solute losses through volatilization. Three different methods were used for measurements of K_D, as described in the following sections.

Method 1

Fifty mL of a freshly prepared feed solution were added to a 125-mL separatory funnel, which was immediately covered with aluminum foil. An amount of undecane, chosen to hold w_E below 1 to 2% w/w, was added by pipette through the aluminum foil. The separatory funnel was agitated for 20 minutes using a laboratory shaker set at 300 rpm. The mixture was allowed to settle for 30 minutes, after which 10 mL of raffinate were transferred by syringe to a stoppered centrifuge tube, which was centrifuged for 30 minutes. Analyses of the raffinate and original feed were made by injecting 5 to 7 repeated 1.0 µL samples by syringe into a Varian Model 1700 gas chromatograph equipped with a flame-ionization detector and a Porapak R column, 0.32 cm in diameter and 0.92 m long.

The definition of K_D is

$$K_D = w_E/w_R \tag{1}$$

and a mass balance gives

$$w_F W = w_E S + w_R W \tag{2}$$

where w_E, w_R and w_F are the weight fractions of the solute in the extract, raffinate and aqueous feed, respectively, and S and W are the masses of solvent and water phases, respectively. Combining Eqs. 1 and 2 gives

$$K_D = \frac{W}{S} \frac{(w_F - w_R)}{w_R} \tag{3}$$

through which K_D was computed. w_R was much less than w_F, lending accuracy to the method.

This method was used for the most soluble and least volatile solutes, for which raffinate concentrations were high enough to be measured with precision by direct aqueous-phase injection.

Method 2

This method was used for solutes with lower solubilities, which were more volatile and led to lower raffinate concentrations. The equilibration procedure was the same as in Method 1, except that the feed solute was added to the separatory funnel by syringe under the liquid-liquid interface of measured portions of undecane and water, which were already present. This obviated any need for the solute to be initially fully soluble in the aqueous phase. Losses of solute by volatilization were percentwise greatly reduced by the large solute-holding capacity of the organic phase, which was present at all times after the solute was added.

After agitation and settling, a portion of extract was transferred to an empty centrifuge tube, and a portion of the raffinate was transferred by syringe,

being released below the extract phase in the centrifuge tube. Again the solvent capacity reduces the importance of any losses of solute by vaporization. In Method 2 organic phases were analyzed, using the same chromatograph and detector, but with a column of 3% OV-101 on Chromasorb W, 0.32 cm in diameter and 1.83 m long. This column gave little tailing of the peak for undecane, enabling satisfactory resolution of the solute peak from it. The extract was injected directly to give w_E. The raffinate was subjected to a second, quantitative extraction, using a mass ratio of undecane to water sufficient to give essentially complete transfer of the solute to the undecane phase. This extraction was carried out in the same way as the first extraction, and the extract from it was analyzed in the same way as the first extract. Denoting variables for the second extraction with an asterisk, and replacing w_F in Eq. 2 by w_R (from the first extraction) gives

$$w_R = w_R^* + \frac{w_E^* S^*}{W^*} = w_E^* \frac{1}{K_D} + \frac{S^*}{W^*} \tag{4}$$

if Eq. 1 is used to relate w_E^* and w_R^*. Substituting Eq. 4 into Eq. 1 then gives

$$K_D = \frac{W^*}{S^*} \frac{w_E}{w_E^*} \left(1 - \frac{w_E^*}{w_E} \right) \tag{5}$$

By virtue of the quantitative extraction, w_E^*/w_E was always much less than unity. Use of Eq. 5 allowed calculation of K_D from the ratio of the measured w_E^* to the measured w_E.

Method 3

This method was used for most of the chlorinated-hydrocarbon solutes, and differed from Method 2 only in that a Ni^{63} electron-capture detector was employed. The electron-capture detector is selectively sensitive to the chlorinated compounds and gave essentially no response to the undecane peak. The extract samples were diluted to the extent necessary to place them in the linear range

for the electron-capture detector. In method 3 isooctane (2,2,4-trimethylpentane), obtained in high-purity form from Burdick & Jackson Co., was used for the dilutions and for many of the quantitative extractions of the first raffinates. In these cases the $1/K_D$ term in Eq. 4 was safely negligible, so that no assumption concerning the value of K_D for extraction into isooctane was needed.

More complete information on the experimental methods is given elsewhere (Barbari, 1981).

EXPERIMENTAL RESULTS

Experimental results are given in Table 5-1, along with the method used, the number of measurements, and the average deviation among measurements. The solutes are arranged in order of increasing values of K_D. More complete data are available elsewhere (Barbari, 1981).

DISCUSSION

Several authors--see, e.g., Banerjee, et al. (1980)--have discussed the relationship to be expected between partition coefficients and aqueous solubilities. For sparingly soluble compounds, the activity coefficient in the aqueous phase (γ_w) is the reciprocal of the mole-fraction solubility in water. The equilibrium distribution coefficient expressed in mole-fraction units (K_D multiplied by the ratio of the molecular weight of undecane to that of water) is simply the ratio of the activity coefficient of the solute in the organic phase (γ_s) to γ_w. Therefore γ_s can be computed from the experimental values of K_D and reported values of solubilities in water. Values of γ_s calculated in this way using solubilities reported by Banerjee, et al. (1980) and Hwang and Fahrenthold (1980) lie in the range 1.2 to 4.4, with exceptions only in cases where there is a wide discrepancy among literature values of the solubility. Even in those cases at least one reported value of solubility leads to a value of

Table 5-1. Experimentally Measured Equilibrium Distribution Coefficients for Extraction from Water into Undecane, 295-300 K.

Solute	Experimental Method	No. of Measurements	Mean K_D	Average Deviation
Benzene	2	3	214	4.2%
Toluene	2	2	740	3.4%
Ethylbenzene	2	3	2500	5.7%
Chlorobenzene	2	5	845	4.3%
1,2-Dichlorobenzene	2	4	3030	5.0%
Chloroform	1	4	74.7	4.5%
Carbon tetrachloride	3	4	738	2.0%
1,1-Dichloroethane	1	5	41.0	4.2%
1,2-Dichloroethane	1	4	25.0	2.6%
1,1,-Trichloroethane	3	3	414	3.2%
1,1,2,2-Tetrachloroethane	3	4	110	2.3%
1,2-Dichloropropane	3	3	73.6	1.1%
1,2-*trans*-Dichloroethylene	3	3	119	2.8%
Trichloroethylene	3	4	354	4.1%
Tetrachloroethylene	3	3	2700	4.7%
Bromoform	3	5	127	1.6%

- - - - -

K_D = wt. fraction solute in solvent phase/wt. fraction solute in water phase, at equilibrium and high dilution.

γ_s within the indicated range. This range of γ_s values is in line with an expectation of modest positive deviations from ideality for solutions of the solutes in question in an alkane solvent.

In Table 5-2, values of K_D measured for extraction into undecane are compared with reported values of K_D for extraction into hexane (Sekine, et al., 1973) and heptane (Leo, et al., 1971). There is a general tendency for K_D to decrease with increasing solvent molecular weight, as would be expected if values of γ_s do not vary greatly. In fact, values of the mole-fraction based partition coefficients into hexane, from Sekine, et al. (1973), and into undecane, from the present work, agree within 9%. Therefore the computed values of γ differ by no more than 9%. Extrapolation and interpolation of the data in Table 5-2 gives a basis for predicting K_D in alkane solvents with other molecular weights.

In Table 5-3, measured values of K_D into undecane are compared with reported values of K_D into 1-octanol, taken from Banerjee, et al. (1980), where available. The ratio of K_D values in the right-hand column should equal 0.833 (the ratio of the molecular weights of 1-octanol and undecane) times the ratio of the activity coefficient of the solute in 1-octanol to that in undecane. Since the alcohol solvent is internally associated through self hydrogen bonding, one would expect the value in the right-hand column to be greater than 0.833 for cases where there is no substantial preferential interaction of the solute with 1-octanol as opposed to undecane. This is the case for all solutes but three--chloroform; 1,2-dichloroethane; and 1,1,2,2-tetrachloroethane. These three chlorinated hydrocarbons are those which fit into the Class IV hydrogen-donor hydrogen-bonding category of Ewell, et al. (1944)--namely, molecules having two or three chlorine atoms on the same carbon atom as a hydrogen atom, or one chlorine on the same carbon atom and one or more chlorine atoms on adjacent carbon atoms. These solutes therefore have the capability of hydrogen bonding preferentially with the electro-negative oxygen in the alcohol solvent, and thereby have lower activity coefficients in 1-octanol than in undecane.

Table 5-2. Comparison of Equilibrium Distribution Coefficients from Water into Different Alkane Solvents

Solute	Equilibrium Distribution Coefficient (K_D) from Water into		
	n-Hexane (Sekine, et al., 1973)	n-Heptane (Leo, et al., 1971)	n-Undecane
Benzene	425	266	214
Toluene	1470	922	741
Chlorobenzene	1440	-	845

Table 5-3. Comparison of Equilibrium Distribution Coefficients for Aromatics and Halogenated Hydrocarbons from Water into Undecane and into 1-Octanol

Solute	Undecane	1-Octanol	(Ref.)	Ratio of K_D into Undecane to K_D into 1-Octanol
Benzene	214	160	*	1.33
Toluene	740	196	*	3.8 (?)
		156 - 754	**	
Ethylbenzene	2500	1710	**	1.46
Chlorobenzene	845	838	**	1.01
1,2-Dichlorobenzene	3030	3040	*	1.00
Chloroform	74.7	96	*	0.78
Carbon Tetrachloride	738	650	*	1.14
1,2-Dichloroethane	25.0	34	*	0.74
1,1,1-Trichloroethane	414	357	*	1.16
1,1,2,2-Tetrachloroethane	110	297	*	0.37
Trichloroethylene	354	318	*	1.11
Tetrachloroethylene	2700	409	*	6.6 (?)

- - - - -

* - Banerjee, et al., 1980

** - Leo, et al., 1971

The other chlorinated hydrocarbons listed in Table 5-3 do not have this characteristic, except for trichloroethylene, where apparently the presence of the double bond serves to reduce its hydrogen-donor ability.

The generally high values of K_D for extractions of chlorinated hydrocarbons and aromatics from water into undecane serve to make kerosene and related mixtures attractive solvents for removing these compounds from aqueous effluent streams. The high values of K_D allow relatively low ratios of solvent flow to water flow to be used in an extraction process for water treatment. Low solvent-to-water ratios can be used effectively in certain types of extractors, such as mixer-settlers and reciprocating-plate columns, and low solvent flows serve to reduce costs for solvent regeneration.

SECTION 6

EXTRACTION OF PHENOLS

There exists an abundant body of information in the published literature on the extraction of phenols from water, which has been practiced on a large scale for many years in connection with coke-oven waters from the iron-and-steel industry. For this reason, the goals of the portion of the present study dealing with phenols were to develop data for a few additional solvents which could be of interest, and to examine the published equilibrium data together so as to reach some conclusions on the relative attractiveness of different solvents. Although they are not classified as Priority Pollutants, polyhydric phenols, such as resorcinol and pyrogallol, were included, since they are troublesome environmentally and are difficult to remove from water.

EXTRACTION OF PHENOL INTO TCP

Table 6-1 shows values of K_D measured for extraction of phenol from water into tricresyl phosphate (TCP), with and without various diluents. The diluents were selected to be representative of potentially attractive compounds from various chemical classes. Diluents were used at a level of 3 parts diluent to one part TCP, v/v. Chevron Solvent 25 is a mixture of alkylated aromatics, resembling butylbenzene. It was used rather than an alkane because TCP has only limited solubility (of order 10 % v/v) in alkanes. The data were obtained by the procedure of batch contacting at a solvent/water ratio of 2/1 v/v (Extraction No. 1). Phenol concentrations were measured in both the feed and raffinate aqueous phases, using analysis by liquid chromatography (HPLC). The extract was then contacted with pure water in a volumetric solvent/water ratio of 1/4 (Extraction No. 2), and the resulting raffinate was again analyzed by HPLC. Even though solvent phases were not analyzed directly, an apparent mass-balance non-closure could be determined by assuming an average value of K_D for the two extractions to estimate the composition of the final solvent phase.

Phenol feed concentrations were 2800 to 3900 ppm w/w.

Table 6-1. EXTRACTION OF PHENOL WITH TRICRESYL PHOSPHATE

Diluent	K_D* Extraction No. 1	K_D* Extraction No. 2	Mass Balance Non-Closure (%)**
None	72	69	+2
	74	73	+5
Methyl Isobutyl Ketone (MIBK)	87	79	+5
	82	82	0
2-Ethylhexanol	46	37	+10
	55	41	+14
Chevron Solvent 25	17.2	18.0	0
	16.1	17.0	-2

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* - K_D = equilibrium distribution coefficient = wt. fraction solute in solvent phase/ wt. fraction solute in water phase, at equilibrium.

** - 100 x (Total solute out - Solute in)/Solute in

Table 6-2. EXTRACTION OF RESORCINOL AND PYROGALLOL WITH TCP

Solute	K_D Extraction No. 1	K_D Extraction No. 2	Mass Balance Non-Closure (%)
Resorcinol	11.6	11.8	-1
	11.6	12.4	-3
Pyrogallol	1.47	1.77	-1
	1.46	1.69	-1
	1.53	(3.28)	-7
	1.40	(2.26)	-4

EXTRACTION OF RESORCINOL AND PYROGALLOL WITH TCP

Table 6-2 shows results for extraction of resorcinol and pyrogallol with undiluted TCP. Procedures were the same as for extraction of phenol. Resorcinol (1,3-dihydroxybenzene) was selected as a typical dihydric phenol, and pyrogallol (1,2,3-trihydroxybenzene) was selected as a typical trihydric phenol. Feed concentrations were 2900 to 3100 ppm w/w.

Because of the tendency of solutions of pyrogallol to darken through light-catalyzed and/or oxidative reactions, these experiments were carried out in a dark vessel under a nitrogen atmosphere. For the two experiments for which K_D for the second extraction is enclosed in parentheses, the pH of the second raffinate was unusually high (about 10), suggesting some degradation of the pyrogallol.

EXTRACTION OF RESORCINOL AND PYROGALLOL WITH ALAMINE 336

Alamine 336 (General Mills, Inc.), a mixture of tri-C_8 to C_{10} amines, was investigated as an extractant for resorcinol (1,3-dihydroxybenzene) and pyrogallol (1,2,3-trihydroxybenzene). Tertiary amines have proven very effective for extraction of acetic acid from water (Ricker, et al., 1979, 1980). Alamine 336 was used at 50 % v/v concentration in several diluents, including 2-ethylhexanol (2EH), kerosene, Chevron Solvent 25, and diisobutyl ketone (DIBK). Results are shown in Table 6-3. From these, it can been seen that K_D is a strong function of the diluent employed, with 2EH as diluent giving the highest value of K_D for resorcinol. However, values of K_D measured for extraction into pure 2EH (also shown in Table 6-3) are nearly as large, thereby indicating that the benefit from complexing the phenols with the amine is not great. Exploratory results obtained with commercial primary and secondary amines did not show any advantage in K_D over the tertiary-amine mixture.

Values of pH for the aqueous phase in the present work were in the range 6 to 8. Sharkov, et al. (1974) report K_D for pyrocatechol (1,2-dihydroxy benzene)

extracted into mixtures of tri-n-octyl amine and kerosene decreasing as pH increases above 2. It may be that amine extractants in the present work would have given higher values of K_D at lower pH.

In the amine-extraction experiments the solutions tended to discolor readily. For this reason later experiments were conducted in the absence of light under a nitrogen atmosphere. This reduced, but did not eliminate, the darkening phenomenon. Measured values of K_D were somewhat lower in the absence of light and under N_2, but not greatly so--20% at most. In Table 6-3, the values reported for 2EH diluent and pure 2EH were obtained under N_2 and in the absence of light, those for kerosene diluent were obtained under N_2 in room light, and those for Chevron 25 and DIBK diluents were obtained under ambient conditions. In all cases, a negative non-closure of the solute mass balance was found, ranging from 0 to 8% and corresponding to disappearance of solute. Furthermore, values of K_D computed for the initial extraction of solute from water into the amine solvent phase were invariably lower than those computed for subsequent back-extraction of the solute from the amine solvent phase into water. The difference ranged from about 20% for 2EH and DIBK diluents to factors of about 4 and 11 for Chevron Solvent 25 and kerosene diluents, respectively. Values reported in Table 6-3 are for the initial extraction from water into the solvent, and are based upon measured compositions of the aqueous feed and raffinate. The mass-balance discrepancy, the discoloration, and the difference in K_D values all indicate the formation of a reaction product from the phenolic solute and the amine, with that product distributing preferentially into the organic phase. This, in turn, suggests an irreversible loss of amine, which would be a severe economic penalty for a water-extraction process. For this reason and because of the unencouraging values of K_D, extraction of phenols by amines was not pursued further.

More encouraging results were reported by Pollio, et al., (1967)

Table 6-3. EXTRACTION OF RESORCINOL AND PYROGALLOL WITH DILUTED ALAMINE 336 AND WITH 2-ETHYLHEXANOL.

Solvent	Aqueous-Phase Solute Concentration (ppm)	Average Value of K_D
Extraction of Resorcinol		
Alamine 336/2EH	450	4.0
Alamine 336/DIBK	500	3.2
Alamine 336/Chevron 25	2300	0.8
Alamine 336/kerosene	2300	0.6
2-Ethylhexanol	1140	3.7
Extraction of Pyrogallol		
Alamine 336/2EH	2100	0.9
2-Ethylhexanol	2300	0.72

Table 6-4. K_D FOR RESORCINOL EXTRACTED INTO ALAMINE 336/2EH, AS A FUNCTION OF SOLUTE CONCENTRATION AND AMINE LOADING*

Concentration of Resorcinol in Aqueous Phase (ppm)	Amine Loading (% of Stoichiometric)	K_D
250	2.1	6.1
450	3.6	5.8
750	5.7	5.8
1000	7.4	4.8
1700	11.6	4.7

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* - under ambient conditions

for extraction of phenol by amine extractants with and without various hydrocarbon diluents. They report K_D = 58 for extraction of phenol by Amberlite XLA-3, a mixture of C_{13} to C_{22} primary amines. However, examination of their results for cyclic reuse of the amine extractant indicates that they too may have encountered loss of phenol and/or amine through a degradation reaction.

Table 6-4 shows values of K_D measured for extraction of resorcinol into Alamine 336/2EH as a function of both the aqueous-phase concentration and the stoichiometric loading of the amine with extracted resorcinol. A mild stoichiometric effect is apparent.

More details on these experiments are available elsewhere (Bell, 1980).

EXTRACTION OF PYROGALLOL WITH TOPO

Trioctyl phosphine oxide (TOPO) is known to complex strongly with phenol and has also been found to have good extractant properties for acetic acid (Helsel, 1977; Ricker, et al., 1979). TOPO is used on a large scale in the hydrometallurgical industry, and presently has a cost around $15/kg ($7/lb).

Table 6-5 shows results for extraction of pyrogallol with a solvent composed of 25 wt. % TOPO in diisobutyl ketone (DIBK). A diluent is needed to put the solid TOPO into solution, and may also be helpful for solvating the reaction complex formed between TOPO and phenols; however DIBK may not be the best diluent from a volatility standpoint. Its boiling point is 168°C, which is close to those of dihydric phenols and lower than those of trihydric phenols. Ketones have been found to be effective for solvating the complexes formed between TOPO and acetic acid.

The values of K_D shown in Table 6-5 are surprisingly high, considering the strong water affinity of the trihydric phenol. TOPO has been explored further as an extractant for phenol, dihydric and trihydric phenols in subsequent unpublished work in our laboratory, falling outside this project,

Table 6-5. Extraction of Pyrogallol with TOPO/DIBK

Feed Concentration, ppm w/w	K_D	
	Forward Ex.	Back Ex.
3080	101	109
3080	107	110
3100	116	123
3100	118	117

and has been found to give high values of K_D in all cases, with possibilities also existing for fractionation between isomers. Among isomeric polyhydric phenols, the highest K_D values tend to occur for those compounds where the hydroxyl groups are adjacent on the ring, indicative of a strong complex involving more than one hydroxyl group. The high values of K_D, although apparently reversible, suggest that regeneration of TOPO may be difficult.

COMPARISON OF ALTERNATIVE SOLVENTS FOR EXTRACTION OF NON-SUBSTITUTED PHENOLS

Table 6-6 shows values of K_D reported in the literature for extraction of phenol by various solvents. Tables 6-7 and 6-8 show similar data for resorcinol and pyrogallol, respectively. In all cases MIBK, a low-boiling solvent, gives the most favorable values of K_D among those solvents considered. MIBK is reported to be the solvent in the Chem-Pro process for extraction of phenols. It gives values of K_D that are considerably superior to those for diisopropyl ether (the solvent in the Lurgi Phenosolvan process), particularly for the polyhydric phenols. In Table 6-6, TCP, Amberlite XLA-3, n-octanol and n-decanol are high-boiling solvents, although the boiling point of n-octanol is close to that of phenol and the system may form an azeotrope.

EXTRACTION OF SUBSTITUTED PHENOLS

Table 6-9 shows results from the present work for extraction of 2-chlorophenol and 2-nitrophenol from water into tricresyl phosphate and undecane. The data for 2-chlorophenol may be compared with the results shown in Table 6-10, which have been reported in previous studies using other solvents.

The much higher value of K_D for extraction of 2-chlorophenol into MIBK than into the other solvents is indicative of a relatively strong complex formation between MIBK and 2-chlorophenol. K_D for extraction of 2-nitrophenol into MIBK is lower, but is still high enough to be indicative of significant complexation. MIBK is an attractive low-boiling solvent for extraction of these two substituted phenols.

TABLE 6-6. REPORTED VALUES OF K_D FOR EXTRACTION OF PHENOL, AT HIGH DILUTION

Solvent	Temperature (K)	K_D	Source
Methyl isobutyl ketone	298	110	(1)
	303	90	(2)
n-Butyl acetate	298	65	(1)
	293	55	(3)
	298	62	(4)
	298	56	(8)
Diisopropyl ether	298	33	(1)
	293	40	(3)
	298	40	(5)
	298	36.5	(6)
	298	42	(7)
n-Octanol	293	38	(3)
	298	48	(5)
	298	48	(7)
n-Decanol	293	32.5	(3)
	298	33	(5)
Tricresyl phosphate	298	72	Present
Amberlite XLA-3	298	58	(8)

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References

1 - Won & Prausnitz, 1975
2 - Burns, 1979
3 - Korenman, 1972
4 - Medir & Mackay, 1975
5 - Kiezyk & Mackay, 1971
6 - Greminger & King, 1979
7 - Luecke, 1979
8 - Pollio, et al., 1967

Table 6-7. REPORTED VALUES OF K_D FOR EXTRACTION OF RESORCINOL, AT HIGH DILUTION

Solvent	Temperature (K)	K_D	Source*
Methyl isobutyl ketone	298	15.2	(1)
	298	17.9	(6)
n-Butyl acetate	298	9.9	(1)
	293	7.0	(3)
	298	9.0	(7)
Diisopropyl ether	293	2.6	(3)
	298	2.1	(6)
	298	2.1	(7)
n-Octanol	293	7.3	(3)
	298	9.9	(7)
2-Ethylhexanol	298	3.7	Present
n-Decanol	293	5.4	(3)
Tricresyl phosphate	298	11.8	Present

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* - See Table 6-6.

Table 6-8. REPORTED VALUES OF K_D FOR EXTRACTION OF PYROGALLOL, AT HIGH DILUTION

Solvent	Temperature (K)	K_D	Source*
Methyl isobutyl ketone	298	3.6	(6)
n-Butyl acetate	298	1.8	(7)
n-Octanol	298	1.4	(7)
2-Ethylhexanol	298	0.72	Present
Tricresyl phosphate	298	1.5	Present
TOPO/DIBK	298	(110)**	Present

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* - See Table 6-6.

** - K_D will depend upon stoichiometric ratio of TOPO to pyrogallol.

Table 6-9. Values of K_D Measured Experimentally for Extraction of 2-Chlorophenol and 2-Nitrophenol from Water into TCP and Undecane

Solute	Solvent	Raffinate Concentration (ppm, w/w)	K_D Forward	K_D Back
2-Chlorophenol	TCP	43-48	890	990
		37-46	1150	920
2-Chlorophenol	Undecane	1550	10.3	-
		1460	11.1	-
		1480	10.9	-
2-Nitrophenol	TCP	48-49	210	200
		52-53	195	185

Table 6-10. Values of K_D for Extraction of 2-Chlorophenol Indicated from Previous Studies

Solvent	K_D	Source
Methyl isobutyl ketone (MIBK)	490	Won & Prausnitz (1975)
n-Octanol	175	Banerjee, et al. (1980)
n-Octanol	170	Leo, et al. (1971)
Methyl decanoate	25	Leo, et al. (1971)
Oleyl alcohol	20	Leo, et al. (1971)
Cyclohexane	0.26	Leo, et al. (1971)

SECTION 7

EXTRACTION OF ACROLEIN

EXPERIMENTAL PROCEDURE

Aqueous feed solutions were prepared by adding 1.00 mL of liquid acrolein to 200 mL milli-Q grade distilled water, making a solution of about 4190 ppm w/w acrolein. In each extraction, 50 mL of feed solution was contacted with 20 mL of solvent and agitated for 25 min. at 300 rev./min. in an automated shaker. The mixture was allowed to settle for one hour, and then the raffinate was centrifuged for one hour. A Varian 1700 gas chromatograph, with a flame-ionization detector and an 0.92-m Porapak R column, was used for analysis. Care was taken to avoid solute loss by vaporization, as was done for the experiments with chlorinated hydrocarbons.

For two extractions, material-balance closures were calculated by analyzing the food solution, the raffinate and the extract. The solvent in both cases was di-n-butyl ether. Material-balance closures, calculated as [100 x (acrolein in raffinate + extract)/(acrolein in feed)], were 99.87 and 98.33%. These results were taken to be a good indication that solute vaporization had been satisfactorily suppressed.

SELECTION OF SOLVENTS TO BE TESTED

In the acrolein molecule there are two potentially active sites for association--an aldehyde group and an olefinic bond. The oxygen atom in the aldehyde group is electron-rich, a fact which points to solvents which have electron-accepting (acidic) sites. Acidic functional groups include the hydroxyl (-OH), carboxylic (-COOH), and nitro ($-NO_2$) groups. The hydrogen in the aldehyde group and the olefinic bond may also have acidic properties which may be satisfied by basic solvents such as ketones, phosphates, amines and ethers. Hence a wide variety of solvents was tested.

EXPERIMENTAL RESULTS AND DISCUSSION

Experimentally measured values of K_D for extraction of acrolein into various solvents are shown in Table 7-1. The only literature value found for comparison is K_D = 1.29 for extraction into toluene (Blazek, et al., 1972).

Measurements were also made with methylene chloride and chloroform as solvents. At the gas-chromatograph operating conditions used, methylene chloride could not be separated well from acrolein. Analyses of the aqueous phase following extraction of acrolein from water with chloroform produced a double peak for acrolein. The second peak was not attributable to chloroform itself, and was probably indicative of some sort of chemical reaction which leaves a product in the aqueous phase. Even counting the entire double peak as acrolein, and assuming a single FID response factor, the values of K_D computed for extraction into chloroform were 0.05 and 0.02. Because of these low values and the apparent reactivity, and because they pose environmental difficulties of their own, chlorinated hydrocarbons were not pursued further as solvents.

One simple test of extraction (or complexing) reversibility is a back extraction following a forward extraction. Complications such as irreversible, slow reactions or solute degradation will tend to make the apparent K_D (still expressed as wt. fraction in solvent phase divided by wt. fraction in aqueous phase) for the back reaction greater than the apparent K_D measured for the forward reaction. For this reason, back extractions were carried out in several cases, using the same contacting conditions as for the forward extractions. For MIBK, the measured K_D for back extraction was 4.0. This value is somewhat <u>smaller</u> than that for the forward extraction and therefore indicates that reversibility is not a problem with MIBK. In the cases of solvent mixtures consisting of 5,5-dimethyl-1,3-cyclohexanedione in 2-ethylhexanol and DIBK, measured values of K_D for back extractions were greater than those found for forward extractions by factors of 1.5 to 8, indicating that a slow reaction, degradation and/or irreversibility occur in those cases. The scattered high values

Table 7-1. MEASURED VALUES OF K_D FOR EXTRACTION OF ACROLEIN FROM WATER INTO VARIOUS SOLVENTS

Solvent	Measured K_D
Alcohols:	
2-Ethylhexanol	1.25
2-Ethyl-1,3-hexanediol	1.41, 1.59
Carboxylic Acids:	
2-Ethylhexanoic acid	0.45, 0.59
Naphthenic acids	0.62, 0.62
Alkane:	
Undecane	0.47, 0.41
Aromatics:	
Toluene	2.05, 2.25
Styrene	2.46, 2.53
Nitrobenzene	2.68, 2.58
Olefins and Terpenes:	
1,5-Cyclooctadiene	0.54
Turpentine	0.39, 0.43
Esters:	
n-Hexyl acetate	1.99, 2.17
n-Butyl acetate	2.38, 2.75
Ether:	
di-n-Butyl ether	1.06, 1.09
Ketones:	
Methyl isobutyl ketone (MIBK)	4.90, 4.91, 4.84
Mesityl oxide	3.01, 5.02
Diisobutyl ketone (DIBK)	1.57, 1.63
5,5-dimethyl-1,3-cyclohexanediond:	
-saturated in 2-ethylhexanol	6.78, 5.9, 3.15
-saturated in DIBK	2.66, 2.15
Furan:	
2-Methyl furan (99% purity)	2.66, 2.23
2-Methyl furan, with up to 10% methyl tetrahydrofuran	8.4, 17.4, 9.29
Phosphoryl Compounds:	
Tributyl phosphate (TBP)	1.97, 1.99
Tricresyl phosphate (TCP)	1.77, 1.68
Di-2-ethylhexyl phosphoric acid	1.72, 1.04
22.1% w/w trioctyl phosphine oxide (TOPO) in DIBK	2.06, 1.63

of K_D for forward extractions using the less pure 2-methyl furan were accompanied by apparent K_D values for back extraction that were about twice as large as those for forward extraction. On the other hand, with the 99% pure 2-methyl furan solvent, K_D values for back extraction (2.23, 2.09, 2.79, 2.87) were close to those for forward extraction. Thus the impurity in the less pure 2-methyl furan seems to provide irreversibility and/or degradation of acrolein.

The carboxylic acids provide relatively low values of K_D, which indicates that interaction with acrolein through their acidity does not offset the lowering effect on K_D which would come from dimerization of the acids in the solvent phase. The alcohols give higher values of K_D. They also can self-associate in the solvent phase through hydrogen bonding, but do have both acidic and basic properties for interaction with the solute. Alkanes have no appreciable capabilities of acid/base interaction, and n-undecane gives a low value of K_D, as would be expected.

On the other hand, the aromatics are one of the few classes of solvents to give values of K_D for acrolein above 2. This indicates that effective pi-electron complexes are formed with acrolein. Unfortunately, most aromatics have undesirable environmental qualities themselves and would for that reason probably not be favored as solvents for treatment of effluent water streams.

Olefinic and terpenic solvents were tested to see if their pi-bonding character would be sufficiently effective. The results were similar to that for the alkane, n-undecane, and are therefore not encouraging.

The Lewis-base solvents--ketones, esters and furans--give surprisingly high values of K_D, indicating that these electron-donor substances interact with the olefinic bond and/or the aldehydic hydrogen in acrolein as electron acceptors. Ethers are less effective bases than esters and ketones, and this is reflected in the relative K_D for dibutyl ether. Among the ketones, the one of lowest molecular weight (MIBK), as expected, shows the highest K_D. The ketones give somewhat higher values of K_D than do esters of equivalent molecular weight or water solubility.

The relatively high solubility of MIBK in water (1.9% w/w) would require that an extraction process include a step for removing residual MIBK from the raffinate water. This would probably be accomplished by atmospheric or vacuum steam stripping. Use of a higher ketone as solvent would give a lower value of K_D but a lower solubility of the solvent in water. For ketone solvents in the C_9 and higher range, recovery of dissolved solvent would probably not be necessary from an economic standpoint, and the raffinate water could then be released directly to a biological treatment unit. Examples of commercially available higher ketones include diisobutyl ketone (K_D for acrolein = 1.60, Table 7-1), isobutyl heptyl ketone and methyl nonyl ketone ("Doggie 'No'").

Mesityl oxide (MIBK with one olefinic bond) is readily available commercially. However, its solubility in water (3%) is greater than that of MIBK (1.9%), and it does not give a higher value of K_D than MIBK. The β-diketone (5,5-dimethyl-1,3-cyclohexane dione) is not of interest because of the apparent irreversibility or degradation of acrolein. 2-Methyl furan gives K_D comparable to those of the ketones, but the purity of commercial solvents could be a problem there.

Phosphoryl compounds tested included a phosphoric acid, a phosphine oxide and phosphates. None appear to offer advantages that would offset their higher cost. Di-2-ethylhexyl phosphoric acid (D2EHPA) was also tested in mixtures with undecane. Except for a case where the D2EHPA extractant had been washed with NaOH solution, this solvent mixture showed no synergistic effects. The amount of NaOH used for the basic wash was stoichiometrically equivalent to about 3% of the D2EHPA. If there were some residual NaOH in the washed solvent mixture, it might react with acrolein to form sodium acrylate.

Extraction of Acrolein with Amines

A number of commercial amine mixtures were tested as potential extractants for acrolein. In each case the amine was diluted to 50% v/v in DIBK. Quite high values of K_D, in the range 100 to 350, were found for the standard contacting

and settling conditions when primary (Primene JMT, Rohm & Haas) and secondary (Adogen 283, Sherex-Ashland Chemicals) amines were used. Values of K_D for extraction with a tertiary amine (Adogen 364, Sherex-Ashland Chemicals) were much lower (1.88 and 2.17). It is known that primary and secondary amines can react with acrolein and/or other carbonyls under appropriate conditions (Sykes, 1971; Mannich, et al., 1936).

Back extractions were carried out for the primary and secondary amine solvent mixtures with DIBK. These showed much higher apparent values of K_D (400 to 800) for the back extractions than for forward extraction. This behavior is strongly suggestive of an irreversible reaction and/or degradation of the acrolein. In the latter case, there would presumably be loss of extractant, as well. In another set of experiments, both fresh Adogen 283 and Adogen 283 recovered from earlier experiments on the extraction of acetic acid were used. Substantially higher apparent values of K_D were found with the regenerated extractant, by factors of 1.5 to 3. The regenerated amine may have contained amides, formed by reaction with acetic acid, in which case the amides may have been more reactive themselves, or may have catalyzed the reaction of acrolein with the amine and/or degradation of the acrolein. Reducing the stoichiometric ratio of amine to acrolein caused the apparent K_D to increase.

The cumulative results of these experiments in effect rule out further consideration of amines as extractants for acrolein.

Regenerability and Stability of Solvents with Acrolein

These subjects are covered in Volume II.

SECTION 8

EXTRACTION OF ACRYLONITRILE

Consideration of the coordination chemistry of acrylonitrile indicates that it should be a basic solute, capable of interacting with Lewis acids. The basicity comes from the electronic configuration of the cyano- nitrogen atom. At the same time, the olefinic bond should offer possibilities for electron-accepting pi-bonding. One can also expect that acrylonitrile could function as a Lewis base, or electron donor, because of pi bonding from the olefinic bond and/or the cyano- triple bond between carbon and nitrogen. For this reason exploratory measurements of equilibrium distribution coefficients have considered both Lewis-acid and Lewis-base solvents.

The experimental procedure used was adapted from that used for extraction of acrolein. Changes were necessitated by acrylonitrile being on the OSHA list of suspected carcinogens. The extraction and analytical conditions were similar to those for acrolein, the only difference being that feeds for the acrylonitrile runs were prepared by adding 1 mL acrylonitrile to 250 mL Milli-Q water to make a 3200 ppm solution (w/w). Pure acrylonitrile was handled in a glove box fitted with appropriate filters. Disposable pipettes, lab coats and gloves were used to eliminate contamination and exposure while handling acrylonitrile. Plastic separatory funnels were used for extractions to reduce chances for spillage or breakage. Liquid wastes were collected, labelled and disposed of with the help of the Environmental Health and Safety office (EH&S) of the University of California. The operating procedures were reviewed in advance with EH&S, and EH&S personnel conducted an exposure test (with negative results) during normal experimental procedure.

Table 8-1 shows results of K_D measurements made for extraction of acrylonitrile from water into a number of solvents and solvent mixtures. From these results one can infer the utility of various molecular-chemical characteristics for extraction of acrylonitrile.

TABLE 8-1. Experimentally Measured Equilibrium Distribution Coefficients for Extraction of Acrylonitrile from Water into Various Solvents and Solvent Mixtures.

Solvent	Measured Values of K_D	
	Individual	Average
Undecane	0.19 0.10	0.15
Toluene	3.49 3.42	3.46
Chloroform	6.54 6.50	6.52
2-ethyl hexanoic acid	1.79 1.51	1.65
2-ethyl hexanol	1.72 1.70	1.71
Nitrobenzene	4.18 4.12	4.15
Methyl Isobutyl Ketone (MIBK)	7.22 6.51	6.9
Diisobutyl Ketone (DIBK)	3.53 3.51	3.52
Tributyl Phosphate (TBP)	5.09 5.44	5.3
n-Hexyl Acetate	3.13 3.80	3.5
Quinoline	3.16 3.24	3.20
50% (v/v) di-2-ethylhexyl phosphoric acid (D2EHPA) in DIBK	2.61 2.55	2.58
50% (v/v) trioctyl phosphine oxide (TOPO) in DIBK	4.28 4.30	4.29
50% (v/v) Adogen 364 (tertiary amine) in DIBK	2.06 2.08	2.07
50% (v/v) Adogen 283 (secondary amine) in DIBK	2.14 2.06	2.10
50% (v/v) Primene JMT (primary amine) in DIBK	2.02 2.15	2.09

Aromaticity: K_D into toluene is relatively high (3.5) in comparison to that into undecane (0.15), indicating that pi bonding with acrylonitrile is effective.

Lewis acidity: Chloroform gives one of the highest values of K_D (6.5), presumably because of donor-acceptor complexation between the electropositive hydrogen of chloroform and the electronegative nitrogen of acrylonitrile. However, chloroform and other, related chlorinated hydrogen donors are themselves pollutants of concern and for that reason would be unlikely to be used as solvents for water treatment.

On the other hand, the carboxylic acid (2-ethyl hexanoic acid) and the alcohol (2-ethyl hexanol) are both Lewis acids, but give relatively low values of K_D. A probable cause of this is internal association of the solvent molecules in the solvent phase, making the electron-acceptor sites less available to the acrylonitrile solute.

Nitrobenzene gives a somewhat higher value of K_D (4.15) than toluene (3.46), reflecting either the additional contribution of the acidic nitro group or the absence of the extra methyl group present in toluene.

Lewis basicity: The Lewis-base solvents give higher values of K_D than was originally anticipated from an examination of the likely chemical-complexing characteristics of acrylonitrile. The ketones give quite high values of K_D, with MIBK giving a larger K_D than DIBK, because of the greater alkyl weighting in the latter compound. TBP gives a relatively high value of K_D, intermediate between those of the ketones, again reflecting a favorable interaction between acrylonitrile and a Lewis base. Hexyl acetate gives a somewhat lower, but substantial, value of K_D, corresponding to the fact that esters are somewhat weaker Lewis bases than ketones.

Pyridine is known to form a complex with acrylonitrile. Hence

quinoline, which has a structure similar to that of pyridine but is not miscible with water, was investigated. The results show that quinoline does not complex more strongly than the other Lewis bases.

Solvent Mixtures: Various stronger acids and stronger bases were investigated in solvent mixtures with DIBK. D2EHPA with DIBK gives a lower value of K_D than does DIBK itself, possibly because of intermolecular association between the acidic D2EHPA and the basic DIBK in the solvent phase, making both less available for interactions with the acrylonitrile solute. Surprisingly, primary, secondary and tertiary amines all give lower values of K_D in mixtures with DIBK than does DIBK itself. For some reason the very strong basicity of these reagents is not of use, even though the highest K_D values measured were for MIBK, which would appear to interact only as a Lewis base.

TOPO in mixture with DIBK gives only slightly higher K_D than DIBK itself, and gives a lower value of K_D than TBP, which is a weaker electron donor. Again, the stronger Lewis basicity of TOPO seems not to be of help.

Regenerability and Stability of Solvents with Acrylonitrile

These subjects are covered in Volume II.

SECTION 9

EXTRACTION OF NITROBENZENE

Hwang and Fahrenthold (1980) indicate that nitrobenzene would be only moderately removed from water by steam stripping at 9% boil-up. Since nitrobenzene is a Lewis acid, it should be readily extractable by various organic bases, and for that reason K_D values for nitrobenzene with various solvents were measured. Analyses of the aqueous feed and raffinate were made using liquid chromatography (HPLC) with a variable-wavelength detector tuned to the strong UV absorption band of nitrobenzene. A C_{18} μ-Bondapak stationary phase was used, along with a mixed methanol/water carrier. Feed concentrations were 1206 ppm w/w. Data were taken at a constant temperature of 30°C.

Table 9-1 shows measured values of K_D for extraction into undecane, toluene, diisobutyl ketone (DIBK), tributyl phosphate (TBP) and methyl isobutyl ketone (MIBK). As can be seen, back extractions indicated that the extractions are reversible. As another basis for comparison of these results, Banerjee, et al. (1980) report K_D = 81.7 for extraction of nitrobenzene from water into 1-octanol.

The results in Table 9-1 show a very strong effect of complexing between the basic solvents (TBP, DIBK, MIBK) and the acidic nitrobenzene. There also appears to be a strong pi-bonding interaction with the aromatic solvent, toluene. One very surprising result is that DIBK provides a higher value of K_D than does MIBK, despite its greater molecular weight. DIBK thereby becomes quite an attractive low-boiling solvent for extraction of nitrobenzene. TBP seems to be a good high-boiling solvent.

Measurements were also made for extraction of nitrobenzene from water into mixed solvents composed of TBP and undecane. The experimental results are shown in Table 9-2, from which it can be seen that K_D is approximately linear in weight fraction.

Table 9-1. Measured Equilibrium Distribution Coefficients (K_D) at 30°C for Extraction of Nitrobenzene from Water into Various Solvents.

Solvent	Solvent/Feed (v/v)	Feed Concentrations, ppm (w/w)	K_D	Average K_D	Average Deviation
Undecane	0.25	1206	36.2	37.4	2.7%
	0.25	1206	38.7		
	0.25	1206	37.3		
Toluene	0.03	965	352	353	0.1%
	0.03	1206	353		
	0.03	1206	353		
DIBK	0.10	503	277	282	3.5%
	0.10	1206	278		
	0.10	1206	301	(Back Extraction: 290)	
	0.15	1206	270		
TBP	0.10	603	269	288	4.4%
	0.10	603	297		
	0.10	1206	277		
	0.10	1206	289		
	0.10	1206	310	(Back Extraction: 299)	
MIBK	0.05	1206	224	215	3.4%
	0.05	1206	217		
	0.10	1206	204		

Table 9-2. Measured Equilibrium Distribution Coefficients (K_D) at 30°C for Extraction of Nitrobenzene from Water into TBP-Undecane Mixtures.

% Undecane v/v	% Undecane w/w	No. of Trials	Average K_D	Average Deviation
0	0	4	288	4.4%
10	7.8	1	264	-
20	16.0	2	251	4.0%
30	24.6	1	257	-
40	33.7	3	199	3.4%
50	43.2	1	181	-
60	53.3	1	185	-
70	64.0	1	117	-
80	75.3	3	118	5.8%
90	87.3	1	79.5	-
100	100	3	37.4	2.3%

All feed concentrations are 1206 ppm (w/w) nitrobenzene and solvent/water ratio of 0.10 by volume. Calculation of K_D based on triplicate analysis of feed and raffinate phases with HPLC.

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